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A SURVEY OF WHITE WATER CORROSIVITY IN EUROPEAN PAPER MILLS

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INTRODUCTION

This survey was done by one of our students, Martin Hubbe, who was awarded a Watson fellowship to conduct a scientific study in Europe. The report describes the results of corrosion tests on mild steel and brass in white water from paper machines producing newsprint, fine papers, hardboard and linerboard. Linear polarization techniques were used to assess the corrosion rate of these metals.

The report relates the status of paper machine closure in Northern Europe to that found in the U.S. (as given by the National Council of the Paper Industry for Air and Stream Improvement). It shows that white water corrosivity is related to specific papermaking operations, e.g., pH, temperature, alum use rate, etc., which are unique to individual mills. No correlation was found between the degree of closure and corrosion.

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A survey of white water corrosivity in European paper mills

M. A. Hubbe and D. F. Bowers*

ABSTRACT

The corrosivity of paper machine white water in thirty North European paper and board mills is reported. White water corrosivity in this report refers to corrosion rate measurements of mild steel and brass using a polarization resistance technique. White water was recycled more for machines of higher productivity. Papermaking variables such as pH, temperature, and the presence of alum and other additives correlated with corrosivity better than did the amount of discharge observed among all paper categories.

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INTRODUCTION

The reuse of paper machine white water has become an almost universal practice within the industry. Energy costs and environmental restraints on effluent discharge have made some form of this practice mandatory. While the closure of white water systems is becoming a worldwide activity, it is the purpose of this paper to describe the trends observed in a recent survey of north European papermaking operations.

Recycling increases the temperature, fines, dissolved solids and biological activity of the water. These factors influence such papermaking variables as flocculation, sizing, retention, and drainage. Likewise, the corrosivity of the white water is changed. The following survey emphasizes the corrosivity: corrosion rate measurements were made in each of the mills visited.

Several investigators, both U.S. and European, have reported various aspects of white water closure and its effect on corrosivity. A review of their findings has been presented in previous papers (1-2). More recently, Sailas reported on some experiences in the selection of stainless steels for paper machine components (3). At the same conference, Nathan and Piluso reported both corrosion type and its cause in a review of corrosion failures on various papermaking components (4). The people in the waste paper processing and board industry have had perhaps the greatest experience with closed papermaking systems. The effect of aeration, bioactivity, and pH in these systems as well as the suitability and extensive use of stainless steel has been the subject of two recent reports (5-6). The most extensive collection of published data which characterizes white water environments is that reported by the National Council of the Paper Industry for Air and Stream Improvements (NCASI). The NCASI work provides a broad coverage of water reuse practice in board, fine papers, and tissue making categories (7). A somewhat similar survey, with greater emphasis on corrosion and the current status of paper machine closure, is currently underway by TAPPI's Corrosion and Materials Engineering Committee (8).

While specific corrosion experiences in white water systems have been reported from Europe relative to a particular type of paper manufacture, there has been no general overview of white water reuse and corrosion in European papermaking practice among the various categories of paper products. The following discussion describes white water data from 30 paper mills in northern Europe. The data was collected during a ten month tour (1976-77) which was sponsored by the Thomas J. Watson Foundation*.

SURVEY DATA

The white water data is classified according to four major categories of paper production; these are groundwood, wood-free, secondary fiber, and hardboard. The categories indicate the major source of fiber in the stock furnished to the paper machine.

Wood-free systems include those fibers produced by chemical pulping processes, while the hardboard classification is for fiber production by the

*M. A. Hubbe was awarded a T. J. Watson Foundation fellowship to conduct this corrosion study and tour.

thermomechanical pulping (TMP) process. Table I shows the number of mills visited and the paper machines inspected within each category. This distribution shows that the survey data is heavily oriented toward the groundwood and wood-free categories. White water properties (pH, temperature, conductivity, and corrosivity) were measured on over 70 samples during the course of this study. Other data, furnished by mill personnel, included water discharge per oven dried (O.D.) ton of product, machine production rate (O.D. TPD), ash content of the product, and additive rates for alum. A full collection of the data is given in Appendix I.

WATER REUSE: PRODUCT TYPE AND PRODUCTIVITY

The degree of water reuse among the different types of mills is shown in Table II. The data shows each paper machine's production rate (O.D. TPD) and its level of discharge (gal/O.D. ton). A measure of evaluation for this water use data can be cited from NCASI surveys in the U.S. (1971-73) (5). Their work indicates discharge levels of less than 6000 gal/O.D. ton for board and 10,000 gal/O.D. ton for fine and tissue paper. Although only 12 to 13 mills were represented in an NCASI study of each papermaking category, their selection was based on the mill's operating experience as a result of closure.

Two trends are observed in the European operations. Table II shows that the degree of white water recycle is greatest for the groundwood and board categories and it is more prevalent in systems of high productivity. For example, within these categories, 60% of all machines inspected were operating below 5000 gal/ton and 78% of these at production levels greater than 100 O.D. TPD.

In general, discharge levels less than 10,000 gal/ton represented 71% of all machine operations, regardless of category. Only 6 of the 45 machines were operating totally closed (0-2000 gal/ton) white water systems.

TEMPERATURE AND CONDUCTIVITY

The expected increase in temperature and dissolved solids content with greater water reuse is shown in Table III. Average values of temperature and conductivity are shown in the data from 17 groundwood and 12 wood-free paper machines. Insufficient data precluded evaluation of these effects for secondary fibers and hardboard. Dissolved solids concentration is qualitatively indicated by the conductivity data. The relative increase of temperature and conductivity for the European mills practicing greater white water recycle is somewhat lower than that reported for U.S. (7); such comparisons require knowledge of clarification and storage practice which is not available from this survey. In general, the data simply confirm the direction of change in these water properties as a function of closure.

WHITE WATER CORROSIVITY

Corrosion tests by the polarization resistance technique were performed on mild steel and brass in white water samples obtained beneath the fourdrinier wire. Several workers have studied the corrosion of these metals in similar environments (9,10,11). The response of both metals was similar in direction, and the following general trends in white water corrosivity are taken from the white water of the same pH and conductivity range as a function of recycle are shown in Table IV. The range of corrosion rates for any category or level of discharge was small so that the average values are considered appropriate for comparisons. The trend toward higher corrosivity at intermediate levels of discharge in the groundwood category and lower corrosion rates for secondary fiber indicate the complexity inherent to evaluating white water corrosivity over a wide range of papermaking operations. Pulp washing, flow rate, acidity, bioactivity, additives, etc., all affect the kinetics of uniform corrosion. The data show that factors other than level of discharge must be used to access recycle white water corrosivity. This is true even for fully closed systems. For example, high corrosion rates were determined for zero-effluent hardboard mills while that for fully closed paper recycling mills producing corrugating medium (secondary fiber) was quite low.

Within the same category, papermaking practice had an influence on measured white water corrosivity. High corrosion rates were measured in those mills using peroxide as a brightening agent. The corrosion rate of brass was always greater than mild steel in these systems. In the wood-free category, alum addition rate correlated with corrosion. Table V shows the increase in mild steel corrosion with increased alum additions.

In all cases, regardless of category, the corrosion of both metals was pH dependent. The corrosion rate increased significantly in white water below pH 5.0.

SUMMARY

The following general trends were observed in visits to 30 North European paper mills practicing some degree of white water closure.

1. Very few paper mills were operating fully closed white water systems.
2. Greater water reuse was practiced on machines of high production rate.

3. Both temperature and dissolved solids concentration (as measured by conductivity) increased with greater water reuse. The highest temperature found in this survey was 127°F which was in a fully closed hardboard mill.
4. White water corrosivity, as measured by uniform corrosion tests on mild steel and brass, could not be correlated with closure over the entire range of papermaking operations investigated. White water in fully closed hardboard mills was much more corrosive than that of secondary fiber mills, for example.
5. Residuals of peroxide bleach tend to increase corrosion of mild steel and brass. Brass corrosion rates were substantially higher than mild steel.
6. Corrosion rate increased with higher alum additions in the wood-free category.
7. White water pH below 5.0 increases corrosion of mild steel and brass for all paper grades.

EXPERIMENTAL METHODS

Three identical mild steel and/or brass electrodes were used to measure white water corrosivity by a polarization resistance technique described by others (12). The mild steel conformed to the commercial ASTMA-36 grade, while the brass was a 65/35 Cu-Zn composition. The 4 mm diameter by 5 cm (exposed length) probes were ground with 400 grit abrasive paper and rinsed in acetone and distilled water prior to each test.

The white water sample, taken just beneath the fourdrinier wire, was allowed to cool to 22°C in the 250 ml test vessel. Then the probes were submerged in the white water for one hour prior to polarization measurements. (Preliminary trials indicated measurements after one hour exposure times were more reproducible than those taken after shorter times.)

A high impedance millivoltmeter, an adjustable power supply, and a microameter were used to conduct the polarization tests.

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APPENDIX

The data in Tables VI and VII are from white water samples from groundwood mills and from individual paper machines. The five measured parameters were white water pH, electric conductivity, temperature at the collection point, and the corrosion rates of mild steel and brass. The other process information is supplied by the mills. Data are categorized as either from groundwood mills, or by the grade of paper or board product. Within each classification the data are arranged in order of increasing electric conductivity.

Table I. Number of Mills Visited, Paper Machines Inspected, and White Water Samples Analyzed

Paper grade	Mills	Number paper machines	Samples
Groundwood	13	25	40
Wood-free	10	29	30
Secondary	5	5	5
Hardboard	2	3	5

Table II. Water Reuse at Various Paper Production Rates[a]

Paper grade	Discharge rate (gal/O.D. ton) 0-2000	2001-5000	5001-10,000	>10,000
Groundwood	87 167 168	96 180 181 195 206 300 350 370 370 450	40 40 300 330	15 50 100 100 250
Wood-free		450	24 32 40 42 67 120	16 17 24 30 30 42 45 70 155 268 278 467
Secondary	337		58 156	
Hardboard	97 107			

[a]Paper machine data within each column in O.D. TPD.

Table III. White Water Temperature and Conductivity

Discharge level, gal/O.D. ton	Groundwood		Wood-free	
	Temp., °F	Cond., µmhos/cm	Temp., °F	Cond., µmhos/cm
0-2000	127	1161	--	--
2001-5000	120	815	95	585
5001-10,000	90	561	78	987
Greater than 10,000	72	460	70	385

Table IV. Average Corrosion Rate of Mild Steel in White Water*

Paper grade	Level of Discharge (gal/O.D. ton)			
	0-2000	2000-5000	5000-10,000	>10,000
Groundwood	6.9	11.6	16.0	7.8
Wood-free	--	--	11.8	8.9
Secondary fiber	1.3	--	0.8	--
Hardboard	89.0	--	--	--

*Corrosion rate in mpy.

Table V. Alum Additions and Corrosion of Mild Steel in White Water Wood-free Papermaking Category

Alum addition, %	Corrosion rate, mpy
0-0.9	6.7
1.4-1.86	8.9
2.0-2.5	11.6
3.2-3.5	11.9
5.5	19.6

Table VI. Groundwood Mills

pH	Conductivity (micromhos/cm)	Mild steel corrosion (milliinches/yr)	Brass corrosion (milliinches/yr)
4.8	202	11.7	0.668
5.0	310	9.07	--
5.1	354	4.02	0.315
4.7	450	11.9	1.72
4.8	504	5.79	1.21
5.4	600	3.78	1.09
6.0	2040	11.5	0.952

*Each mill uses debarked spruce logs and is integrated with the white water system of paper machines. Samples were filtered prior to corrosion tests.

Table VII. Paper and Board Machines

Grade	pH	Conductivity (μmhos/cm)	°F	Gallons, ton	Tons, day	Mild steel corrosion (mils/yr)	Brass corrosion (mils/yr)	Ash, %	Alum, %
Newsprint	4.8	204	126	2330	350	9.47	1.42	1.0	
	5.4	283	126	2190	96	9.59	0.712	1.0	
	4.6	300	127	3120	3000	9.85	0.717	3.5	
	4.45	431	--	2400	450	10.5	1.37	0.4	
	4.0	740	--	10800	250	2.73	0.123	--	
	6.5	756	131	3000	370	1.01	0.157	6.0	
	6.2	939	131	3000	370	3.12	--	6.0	
	5.8	2660	--	720	--	5.84	0.697	10.0	
	5.5	2730	--	721	--	4.74	--	10.0	
Newsprint: Hydrosulfite-brightened	4.55	300	124	3100	206	16.6	0.599	5.5	
	3.85	389	--	10800	100	6.38	3.55	--	
	3.9	523	--	14400	100	7.62	0.437	22	
	4.9	590	127	1580	168	8.48	1.82	6	
	4.5	620	127	1580	167	5.29	0.452	6	
	5.8	2380	--	720	--	8.02	0.697	15	
Newsprint: Peroxide-brightened	5.1	450	99	6720	330	15.1	0.290	15	
	4.8	600	109	5670	300	29.6	16.8	2	
	4.6	800	64	--	50	26.2	6.14	12	
	5.4	950	104	4800	180	33.8	--	1	
	5.4	1300	95	4800	181	43.0	1.03	1	
Wall paper	4.05	425	--	14400	50	8.44	1.20	12	3.0
	4.1	1300	118	2880	195	27.7	0.889	20	1.5
Folding Boxboard (groundwood ply)	5.5	230	86	--	36	9.35	0.545		
	4.8	284	--	--	90	5.56	1.82		
	5.1	330	95	1100	87	9.39	1.05		
	4.1	505	72	10300	15	13.8	2.14		
	4.1	622	84	7930	40	12.7	1.84		
	3.9	655	72	7920	40	19.3	2.02		

Table VII (Cont.). Paper and Board Machines

Grade	pH	Conductivity (µmhos/cm)	°F	Gallons, ton	Tons, day	Mild steel corrosion (mils/yr)	Brass corrosion (mils/yr)	Ash, %	Alum, %
Folding	4.2	458	73	8410	24	9.71	3.04	0	0
boxboard	5.7	505	90	--	55	11.5	0.604	6	1.5
(wood-free	5.2	788	75	6480	42	12.9	0.628	9	2
ply)	5.5	788	--	6480	40	14.5	0.540	9	2
	5.1	855	70	7930	32	7.84	0.540	--	Yes
	4.9	2550	75	10300	30	15.3	2.14	--	Yes
Wood-free	4.4	330	64	11500	70	8.30	4.19	18	1.4
printing	6.45	565	95	2400	450	0.917	0.191	15	0
	4.2	600	99	14400	155	9.21	3.09	10	2.3
	6.6	605	95	2400	450	1.09	0.221	15	0
	5.4	830	64	11500	70	8.71	0.673	18	1.4
Wood-free	7.0	600	84	10800	278	4.20	1.37	--	0
fine	4.45	820	79	8400	67	10.3	2.50	--	3.5
	4.7	848	109	--	360	6.06	0.432	--	0.9
	4.3	874	79	8400	67	17.3	1.20	--	3.5
	6.3	1560	79	8400	120	27.4	1.12	--	5.5
	4.4	1590	79	8400	120	13.3	1.30	--	5.5
	4.3	1770	79	8400	120	27.4	1.12	--	5.5
	4.6	2380	79	8400	120	10.1	1.09	--	5.5
Machine-	4.1	215	46	10600	17	High	7.66	--	2.2
glazed	4.4	224	50	10600	16	11.1	3.73	--	2.2
(wrapping	4.3	233	--	10600	--	8.66	0.491	--	2.2
paper or	4.2	250	--	10600	17	7.52	1.82	--	2.2
base for	3.9	280	48	10600	24	20.7	--	--	2.2
carbon	4.1	422	--	10600	--	10.1	2.60	--	2.2
paper)	4.5	460	64	11500	30	8.80	2.42	1.5	1.5
	5.7	615	59	11500	45	7.98	0.545	14	3.2
	5.9	730	64	11500	30	8.62	0.717	1.5	1.5

Table VII (Cont.). Paper and Board Machines

Grade	pH	Conductivity (μmhos/cm)	°F	Gallons, ton	Tons, day	Mild steel corrosion (mils/yr)	Brass corrosion (mils/yr)	Ash, %	Alum, %
Tissue	7.5	138	73	16600	42	11.6	0.275		
	9.35	336	--	16800	--	5.65	0.133		
	9.95	556	--	16800	--	3.37	0.491		
Unbleached kraft board	5.5	--	82	10800	268	4.20	1.37	--	2.5
	6.1	--	93	10800	467	7.52	0.344	--	1.86
Secondary fiber products	5.1	200	68	--	36	9.58	--	1.5	
	5.7	326	75	--	164	11.2	1.06	0	
	4.6	552	68	--	100	9.99	1.77	1.5	
	6.4	1130	104	6720	156	0.593	--	--	
	6.4	1140	--	6720	--	1.05	--	--	
	6.2	1200	85	5760	58	0.821	0.285	--	
	5.1	8190	--	Zero	--	0.775	0.614	--	
	5.5	11100	96	Zero	337	1.78	0.957	1.5	
TMP hardboard	3.8	1299	--	--	--	5.15	0.687	--	
	4.4	4370	131	Zero	97	25.1	0.574	--	
	4.5	4405	117	Zero	102	114.0	0.304	--	
	4.5	4980	131	Zero	97	63.8	0.260	--	